

US EPA ARCHIVE DOCUMENT



UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

March 7, 2012

Ronald Zelt  
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**Re: Sampling Plan – Supplemental Recommendations  
Prepared by the Scientific Support Coordination Group (SSCG)  
for Aquatic Toxicity Testing and Oil Fingerprinting  
Enbridge Line 6B MP608 Release, Marshall, MI**

Dear Ron:

I have reviewed the above-referenced letter report containing three (3) supplemental recommendations to the previously submitted Sampling Plan that was prepared in response to Charges 1, 2, and 3 submitted to the SCCG:

Charge 1

- a) Provide an evaluation of viable analytical approaches, including benefits and draw backs for each, to quantify the amount of submerged oil in the Kalamazoo River sediments attributable to the Enbridge Oil pipeline release.

Charge 2

- a) Identify and evaluate viable procedures for assessing the toxicity of remaining submerged oil.
- b) Provide a recommendation for the best procedure to accomplish this goal.

Charge 3

- a) Provide an evaluation of viable procedures, including benefits and draw backs for each, to assess whether remaining submerged oil will biodegrade over time.
- b) Provide a recommendation for the best approach to accomplish this goal.

I hereby accept the group's three (3) supplemental recommendations. Our Environmental Unit and Enbridge have already initiated their implementation. While no additional field work is necessary to accomplish the identified tasks, the required laboratory analyses and data reprocessing are expected to be complete by March 21, 2012. This will allow adequate time for evaluation and interpretation of the results prior to the planned SSCG meeting on March 29-30, 2012.

Once again I must extend my sincere appreciation for the level of professionalism and diligence displayed by the SSCG members. The supplemental recommendations identified by your

subgroup indicate that the SSCG members are highly engaged, reflective, and clearly motivated to assist me in bringing this project to a successful conclusion.

Sincerely,



Ralph Dollhopf  
Federal On-Scene Coordinator and Incident Commander  
U.S. EPA, Region 5

**cc:** L. Kirby-Miles, U.S. EPA, ORC  
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March 2, 2012

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Subject: Sampling Plan - Enbridge Line 6B MP 608, Marshall, Mich., Pipeline Release  
Supplemental Recommendations

Dear Mr. Dollhopf:

With this letter, the Chemistry, Fingerprinting, and Biodegradation Subgroup of the SSCG transmits supplemental recommendations regarding the characterization of oil and oiled sediments in the Kalamazoo River. After considerable discussion the Subgroup recommends three additions to the sampling and analytical plan previously submitted for your consideration. These supplemental recommendations address:

1. Sieving of sediment samples at Alpha Analytical laboratory for oil fingerprinting analyses.
2. Reprocessing of raw data for historical site samples that were analyzed using Method 8270 GC/MS in full scan mode.
3. Overall SARA-fractions analysis of oil samples.

The following text summarizes our evaluations of these three supplemental recommendations.

1. Sieving of Sediment Samples Collected Specifically for Toxicity Tests.

Objective of chemical analyses of these samples is to characterize the hydrocarbons present in the sediment used for toxicity tests; thus, we want to have sample processing for analytical chemistry and toxicity tests be as similar and parallel as we can, without compromising the data quality from either test. U.S. EPA guidance identifies that these samples often are not sieved, and, if sieving is necessary, commonly uses sieves with large mesh openings. However, if the aliquot of each sample being sent for chemical fingerprinting analysis is not sieved, there is the potential that sediment samples with large amounts of leaf litter or other plant material may contribute substances (e.g., plant waxes or alkanes) that might interfere with the analysis of petroleum hydrocarbons. In order to determine whether this plant material is affecting the analysis of PAHs, biomarkers, TEH, and other hydrocarbons, the Subgroup recommends that ten (10) of the recently collected sediment samples be split (from a homogenized composite), and one aliquot sieved using a stainless steel 10-mm mesh sieve. These ten sample aliquots should be otherwise processed and analyzed identically to the unsieved split aliquots. The results of these paired samples (sieved and unsieved) will be compared to determine whether sieving should be included in any subsequent sediment sample processing protocol for this project. Adequate sediment is already present at Alpha Analytical laboratory to accomplish this task; however, it is important for avoiding introduction of extraneous variation that both members of each pair of samples (sieved and unsieved) should be analyzed during the same analytical batch,

so that both samples are extracted at almost the same time, by the same person, and analyzed on the same instrument with a common calibration.

2. Reprocessing of Raw Data for Historical Site Samples.

It is probable that historical GC/MS raw data for samples collected over the past 19 months at the Site may provide additional useful chemistry information beyond the 17 Priority Pollutant PAH levels originally reported. If the appropriate electronic data files (raw data files from laboratory instruments) can be acquired, reprocessing of these data files may allow the identification and semi-quantitation of many of the important constituents used in fingerprinting analyses of petroleum products and for inferring weathering pathways of the products in the environment. In order to determine whether this approach has merit and practical applicability for this Site, the Subgroup recommends a limited study of the electronic data files representing about twenty (20) historical sediment-core samples that contain relatively high levels of previously analyzed PAHs. By re-processing this subset of data, we will be able to determine whether further application of this approach to historical data would likely prove useful to address, with a larger scope, questions such as weathering, biodegradation, and oil quantification.

3. SARA Analysis of Oil Samples.

Previous experience with the very heavy crude oils such as those from Alberta tar sands suggests that a large, but unknown, fraction of the residual oil from Line 6B remaining in the environment is of a heavy molecular weight not directly accessible to the chemical fingerprinting approach being used per the primary analytical chemistry plan recommended previously by the SSCG. The heaviest fractions of crude oil are the resins and asphaltenes, whereas the remaining fractions comprise the saturates and aromatics. The resins and asphaltenes likely are less biodegradable, less bioavailable, and less soluble; they may have less toxicity as a result. Understanding what proportion of the released or weathered oil that the resins and asphaltenes compose is therefore useful for guiding expectations about weathering and degradation, helping understand toxicity, and important for full accounting in mass balance models of the fate of released oil. The Subgroup recommends that aliquots of the five (5) samples of source or weathered oil previously submitted to Alpha Analytical be submitted to a petroleum-industry service laboratory for "Iatroscan" analysis of SARA fractions (standard method IP-469), to determine all four compound classes by adsorption chromatography. This method is best suited to samples of heavy oil with minimal light-end components. Additionally, for quality control and to aid interpretation of results, samples of two (2) standard or reference crude oils should also be submitted to the same lab for the same method IP-469 analysis. The Subgroup recommends the use of one standard crude oil, such as a light oil from Alberta, similar to Federated; and a reference crude oil sample, such as Cold Lake bitumen.

Based on the Subgroup members' extensive experience working on oil spill related issues, we recommend the adoption of these sampling and analytical plan additions.

On behalf of the SSCG sub-group, very sincerely yours,

/s/

Ronald B. Zelt, P.HWQ.

U.S. Geological Survey